

CATALYSIS OF LOW TEMPERATURE LIQUEFACTION BY MOLYBDENUM SULFIDES

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KEYWORDS: Liquefaction, dispersed catalysts, molybdenum disulfide

INTRODUCTION:

The use of molybdenum sulfide catalysts in the direct liquefaction of coal is well known. Nonetheless, the development and application of more effective catalysts, particularly in first-stage liquefaction reactors, remains a high priority goal¹. When used as unsupported catalysts in first-stage reactors, molybdenum sulfides are often intended to promote the conversion of coal and to provide better quality products for further refining. Typically, temperatures ranging from 400° to 465° C are used in first-stage reactors to promote the formation of distillable products. Molybdenum catalysts used at these temperatures generally increase coal conversion and the yield of distillates, and reduce the content of heteroatoms, principally sulfur and oxygen. Results described below suggest that molybdenum catalysts might play additional roles. The conversion of coal to soluble products at low temperatures, generally around 350° C, may be promoted by active catalysts, possibly through the prevention of retrogressive reactions². With this in mind, the activity of molybdenum catalysts in low temperature liquefaction was investigated. The results indicate that it is of value to have the catalyst present in an active form when the liquefaction feed stock is brought to temperatures above 300° C.

EXPERIMENTAL:

Small-scale liquefaction reactions were carried out in 316 stainless steel autoclaves of about 40 mL capacity. A set of five microautoclaves was heated and shaken (60 cps) in a sandbath. In these experiments, the reactors were brought to temperature slowly by heating the sandbath at about 6° C/min. The usual charge was 3.5 g Illinois No. 6 coal, 7 g coal-derived liquefaction solvent, and 1200 psig hydrogen at room temperature. Larger scale experiments were carried out in a 316 stainless steel stirred autoclave of 1/2 L capacity. Typical charges were 70 g coal, 140 g solvent, and 1200 psig hydrogen at room temperature. The heating rate was about 8° C/min. Rapid cooling was achieved by flowing water through an internal cooling coil.

Coal conversions were calculated on an maf basis from weights of dry residues recovered after vacuum filtration on 8u paper with cyclohexane followed by tetrahydrofuran (THF). The catalyst was added to the coal by mixing it with about 40% of its weight of an aqueous solution of ammonium heptamolybdate or ammonium tetrathiomolybdate followed by drying in a vacuum oven at 60° C. In one case, the catalyst was simply added to the reactor as a powder without impregnation. The coal was from Burning Star mine, and had the following elemental composition: C=78.4%; H=5.1%; N=1.6%; O=11.4% (by diff.) on an maf basis with total S=3.2%. The ash content was 10.4% on a moisture free basis. The liquefaction solvent was a hydrotreated distillate (V-178) obtained from the Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama. Its carbon and hydrogen contents were C=88.2% and H=9.6%. By

D-1160 distillation, 84% distilled below 850° F.

RESULTS AND DISCUSSION:

The use of unsupported molybdenum sulfides as liquefaction catalysts is well known¹. Nonetheless, at the outset of this work, it was useful to establish whether or not catalyst activity could be observed at low temperatures, in this case about 350° C. Two sets of experiments were used to verify catalyst activity. In the first, coal conversion (THF) was measured as a function of catalyst loading. The residence time at liquefaction temperature (350° C) was 60 min. The conversion values shown in Fig. 1 increase with catalyst loading until a plateau is reached at around 2000 ppm molybdenum. Conversions with either ammonium heptamolybdate and ammonium tetrathiomolybdate were generally similar except at the lowest concentration. These differences aside, the more important observation is that the precursors may be activated and perform a catalytic function at low temperature.

In addition to increasing the conversion of coal, a catalyst may be expected to increase the rate of hydrogen consumption. In these experiments, we have no direct, real-time indication of changes in hydrogen partial pressure. However, the microautoclaves were equipped with pressure transducers allowing total pressure to be recorded as a function of reaction time. The time/temperature and time/pressure profiles for a set of autoclaves heated together in the sandbath are given in Figure 2. The pressure increased with temperature, as expected. A peak in total pressure is observed a short time after the temperature reached 350° C. Thereafter, total pressures declined.

The pressure profiles shown result from a composite of the effects of temperature changes, hydrogen uptake, and production of other gases or vapors. Despite this complexity, important information may still be derived from the profiles. Peak pressure developed shortly after reaching liquefaction temperature, indicating that the major portion of gas formation is rapid, being almost complete within several minutes of reaching reaction temperature. Analysis of the gases recovered at the end of the run indicates that the major component of the non-condensable gases evolved is CO₂, with a lesser amount of CH₄. Once gas evolution slows, a gradual decrease in total pressure is observed. This decrease is reasonably attributed to hydrogen uptake. Although the decrease is larger when catalyst has been added, it is evident even when it has not. It is possible that a native catalytic effect of coal mineral matter may contribute to the pressure decrease. Indeed, the Illinois No. 6 coal used in this work has a high iron content (1.1 wt%, mf).

The changes in total gas pressure reflect the effects of both temperature changes and chemical reactions. An attempt to factor out the former was made by estimating the pressure change that would be due to the temperature change. This estimate was based on a least squares fit of the temperature/pressure data using the first three points covering the temperature span from 15 to 219° C. The resulting linear equation was then used to calculate expected pressures for higher temperatures. This estimation assumes that the evolution of gases below 219° C is negligible. The difference between the calculated and observed pressures is a rough estimate of the combined effects of gas production and hydrogen uptake. Pressure differences calculated from the data in Figure 2 are plotted versus time in Figure 3.

The difference between catalyzed and non-catalyzed liquefaction is readily apparent. In the catalyzed cases, the pressure peak is reduced and hydrogen uptake begins to dominate within the first 15 minutes at 350° C. Coal conversions were also somewhat higher, being 91-92% for all catalyzed cases as opposed to 87% without catalyst. By cyclohexane extraction, conversions with catalyst ranged from 12% to as high as 21%

for 5000 ppm Mo. The value without catalyst was only 7%. Clearly the precursor was activated at 350° C and the resulting catalyst played an important role in the early stages of the liquefaction reaction.

The relative rates of hydrogen uptake at times beyond the pressure peak are also interesting. The rates are nearly identical for catalyst loadings of 1000 and 5000 ppm Mo. At these levels, the rate of hydrogenation seems to be limited by factors other than the amount of catalyst present. It is also apparent that the rate of hydrogen uptake falls off with time until it approaches that observed in the absence of added catalyst. This observation was grounds for asking whether or not the catalyst was progressively deactivated.

To determine if the catalysts were in fact deactivated, the tetrahydrofuran insoluble residues recovered after product work-up were mixed with fresh coal slurry and a second cycle of liquefaction was performed. For comparison, simultaneous experiments were made with and without the addition of ammonium molybdate powder. The temperature/pressure-difference profiles are shown in Figure 4. The experimental conditions were the same as the initial liquefaction experiment, except that the temperature was increased to 425° C after 120 minutes at 350° C. The pressure differences were calculated as before. As may be seen in the Figure, catalytic activity is quite apparent for the material recovered from the previous experiment. Improvements in coal conversion were also obtained by using the liquefaction residue. Values determined by THF extraction were 95% with liquefaction residue, 86% with ammonium molybdate, and 85% without catalyst. Measured by cyclohexane extraction, the values were 64%, 36%, and 38%, respectively.

It is important to note that the liquefaction residue demonstrated catalytic activity as soon as the temperature reached 350° C. The recovered catalyst was not only active, but able to participate in liquefaction reactions during the first few critical minutes. A pattern of hydrogen uptake similar to that seen in the previous experiment is repeated here. With added liquefaction residue, the rate of hydrogen uptake diminished with time until it approached that for the non-catalyzed case. However, when the temperature was increased to 425° C, the apparent hydrogen uptake was much greater in the presence of the liquefaction residue. From the results of temperature programming, it seems the catalyst acts as a cofactor in processes that are initiated by thermal reactions. Thus, as the temperature is brought up to each plateau, a new but limited burst of catalyzed hydrogen uptake initiated. These observations are in accord with the concept of catalytically controlled thermal cracking postulated for petroleum residues and other heavy hydrocarbons¹. In that concept, MoS₂ was pictured as hydrogenating thermally produced free radicals, thus inhibiting the formation of coke.

Comparison of the addition of the liquefaction residue with addition of ammonium molybdate in the form of a powder illustrates the importance of dispersing the catalyst precursor. The added ammonium molybdate powder performed only marginally better than coal without added catalyst, even though twice as much molybdenum was added in the form of the powder as in the liquefaction residue. This relatively poor performance most likely resulted because no effort was made to disperse the catalyst precursor. By contrast, the precursor used to generate the catalyst in the liquefaction residue had been dispersed on the coal in the first liquefaction experiment. Thus, a major benefit of dispersing a precursor on coal is that more effective catalysts may be produced. This benefit is separate from any derived by improved contact between coal and catalyst brought about by dispersing the precursor. It should be emphasized that in the second liquefaction experiment, the added catalyst was physically associated with the liquefaction residue from the previous experiment. The degree of contact with fresh coal was then governed by the extent of mixing in the reactor. Experiments directed

toward improving the contact between the coal and catalyst thus need to take into account the effect the chosen method of dispersing the precursor might have on the physical properties of the resulting catalyst. It is also apparent that tailoring the conditions of the preparation of an unsupported catalyst may have a large effect on its performance in a process that makes use of catalyst recycle.

The recovery of the catalytic material in the previous experiments entailed the solvent separation of the liquefaction products. Thus, the catalyst was exposed to several laboratory operations that could have degraded its performance in the subsequent liquefaction cycle. These extraneous influences make it more difficult to conduct a systematic program to improve the preparation of these catalysts. A way around this problem was devised by preparing catalysts under liquefaction conditions in a microautoclave, then transferring them without work-up to a 1/2 L stirred autoclave for performance testing. In this way, a small volume of liquid product containing active catalyst can be mixed with a larger volume of fresh feed slurry before liquefaction. In this testing scheme, the precursor loading in the preparation stage must be high in order to supply enough catalyst for the performance test in the stirred autoclave. Initially, 20,000 ppm of ammonium molybdate on coal was used in the preparation, which reduced to 1000 ppm Mo after dilution with 20 times as much fresh coal in the performance test.

Initial tests of this preparation/testing scheme revealed that the introduction of active catalyst to the stirred autoclave often led to exothermic reactions as the temperature approached about 350° C. In general, the extent of these exotherms varied according to the type and amount of catalyst used. Thus, the temperature profiles were not reproducible. To obtain better control, a temperature staged testing program was adopted. One such temperature profile for a noncatalyzed liquefaction experiment in the 1/2 L stirred autoclave is illustrated in Figure 5. In this example, 20 minutes was spent at 300° C, followed by 60 minutes at 325° C, then 50 minutes each at 350° and 375° C. The total pressure rose until 10 minutes after reaching 325° C. Expected pressures were calculated based on the initial pressure change as done before. The difference between expected and observed pressures is plotted in Figure 6. For comparison, the pressure difference profile for a case with added catalyst is presented in Figure 7. The heating program was closely similar to the non-catalyzed example, but they are not identical. Several important observations may be made by comparing the two pressure difference profiles. First, in the non-catalyzed case, the onset of the pressure peak is evident as the temperature approaches the first plateau, 315° C, and it is much larger in magnitude than in the catalyzed case. This apparent increase in hydrogen uptake is further evidence that the catalyst carried in the liquefaction products of the previous run is able to function during the initial stage of the liquefaction reaction. Second, the pressure difference at the end of the heating program is much more negative with than without added catalyst. Third, the rate of pressure change in the presence of catalyst is nearly constant once the pressure peak has passed. It is striking that the rate of uptake does not seem to be affected by the changes in temperature. This is somewhat different than the profile from the microautoclave experiment shown in Figure 4, which exhibited a distinct change in rate as the temperature increased to the next plateau. It may be that the smaller temperature changes in the stirred autoclave experiment combined with a fortuitous choice of intervals between temperature changes produced a constant rate of uptake.

CONCLUSIONS:

The results obtained in this work indicate several factors are

important to using unsupported molybdenum sulfide catalysts more effectively in the first stage of liquefaction. Since catalysts are able to participate in liquefaction reactions at low temperatures, it is important that they be present in an active form rather than allow this one-time opportunity to pass while a precursor undergoes transformation. One approach to this objective is demonstrated here, namely, preparation of a catalyst from a precursor dispersed on coal in a small reactor followed by mixing the entire liquefaction product with fresh slurry for use in a larger reactor. Impregnation of the precursor on coal seems to be of benefit to generating a better catalyst. Such a prepared catalyst is able to perform well in subsequent liquefaction tests even though it is only physically mixed with coal, not impregnated in any way. It is also clear that evaluation and comparison of liquefaction catalysts is complicated by the fact that performance is governed by many factors, not just catalyst activity. For example, during typical liquefaction experiments, the catalytic properties of a precursor added with the feed undergo considerable change during the course of the reaction. For this reason, the results given above are taken as measures of overall catalyst performance rather than catalyst activity. In the present context, the latter may not be a static characteristic.

ACKNOWLEDGEMENT:

We gratefully acknowledge the assistance of Harold M. Boyer in carrying out many of the liquefaction experiments.

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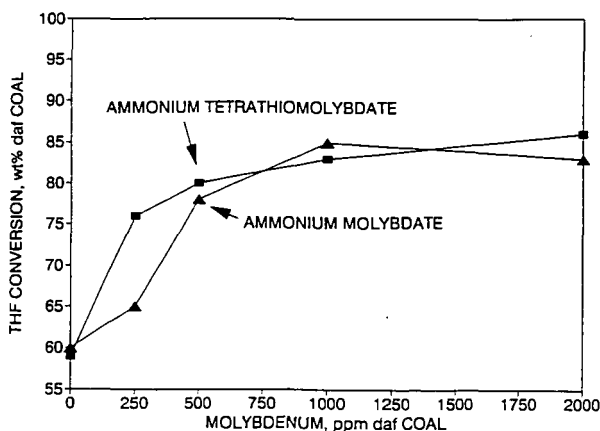


Fig. 1. Conversion versus molybdenum loading.

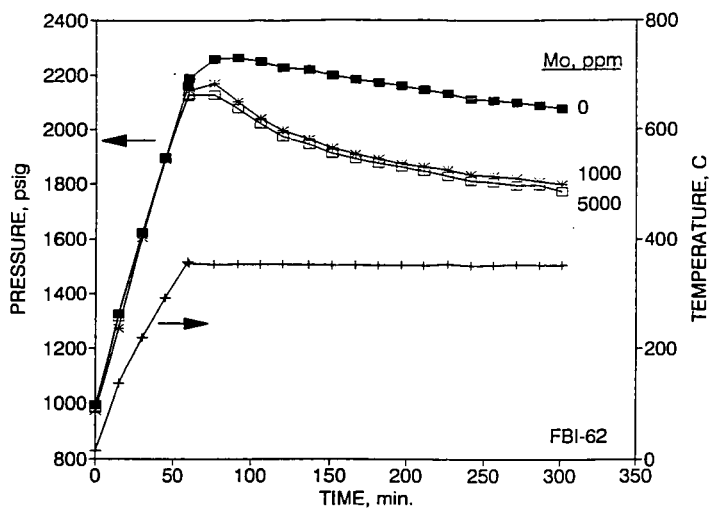


Fig. 2. Temperature and total pressure profiles.

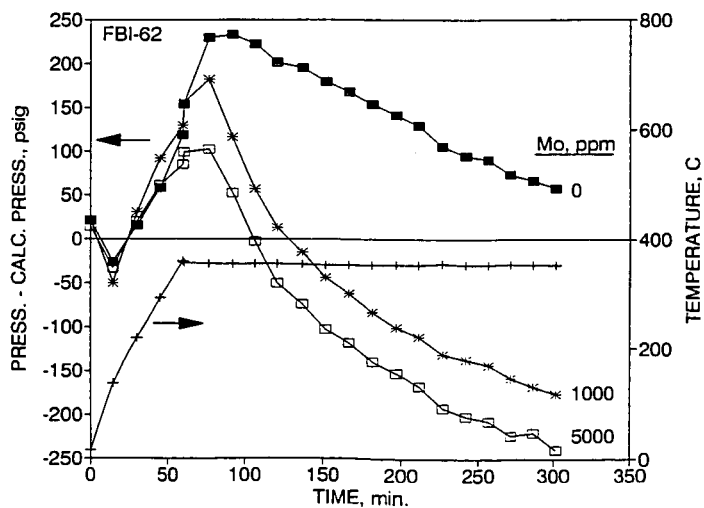


Fig. 3. Differences between calculated and total pressure.

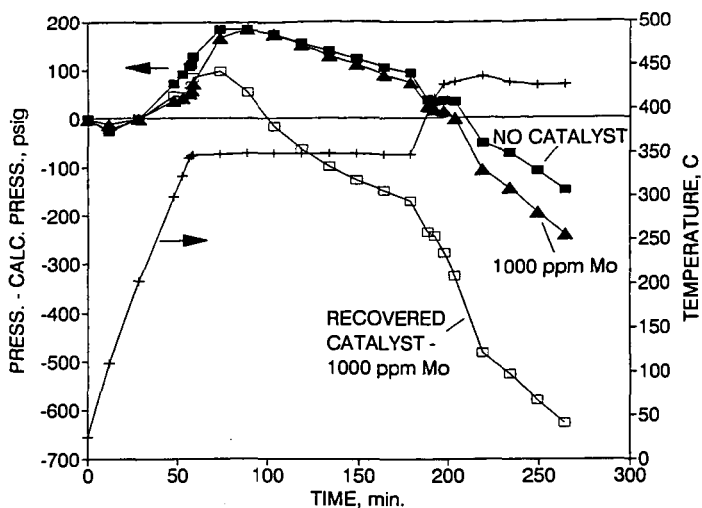


Fig. 4. Pressure difference profiles with and without catalyst.

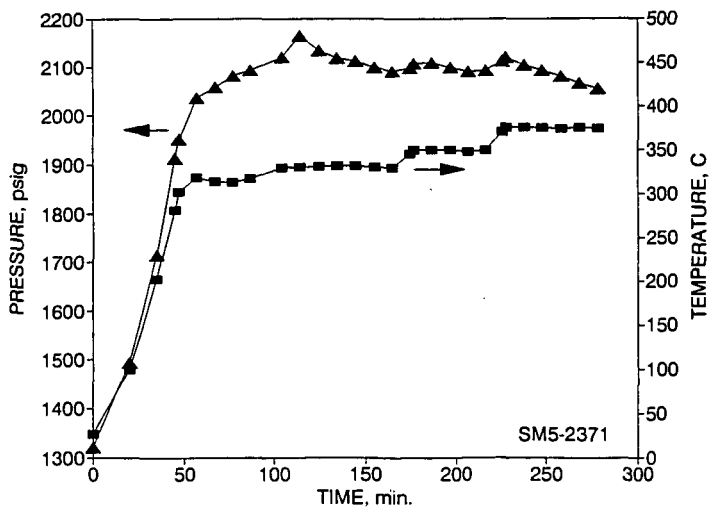


Fig. 5. Temperature and pressure profiles without added catalyst.

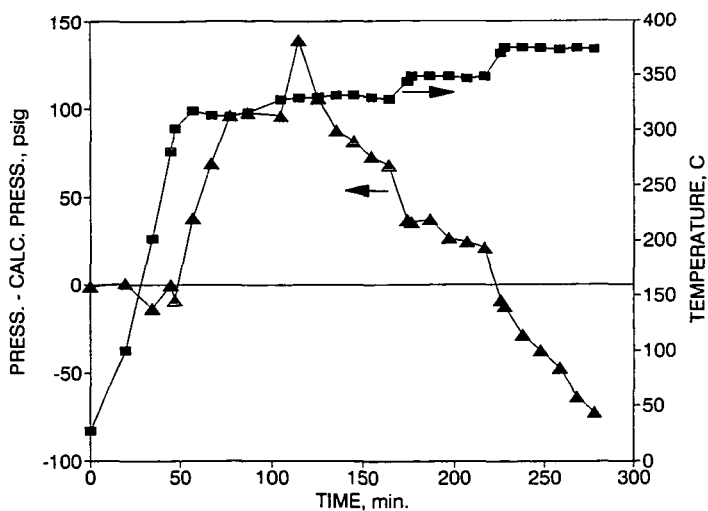


Fig. 6. Pressure difference without added catalyst.

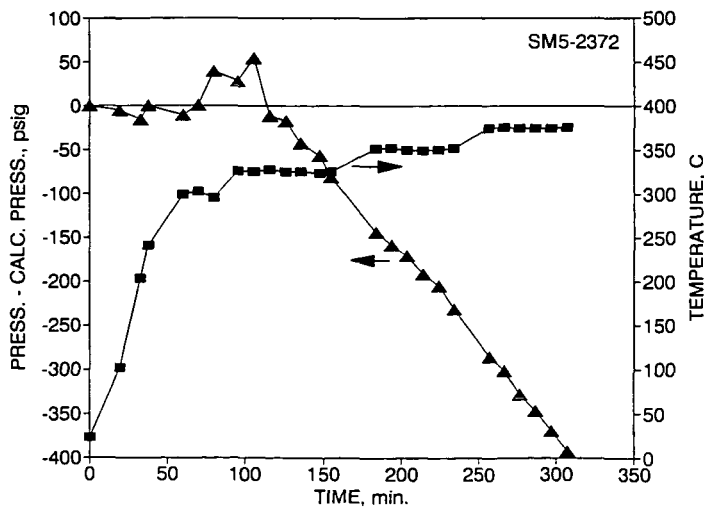


Fig. 7. Pressure difference with 1000 ppm Mo added.